

SELECTION OF A LIQUID CALCIUM-LITHIUM ALLOY FOR FABRICATING CaO INSULATOR COATINGS ON V-5%Cr-5%Ti* J.-H. Park and T. F. Kassner (Argonne National Laboratory)

OBJECTIVE

Electrically insulating CaO coatings have been produced on V-5%Cr-5%Ti by exposing the alloy to liquid Li that contained 0.5-85 wt.% dissolved Ca at 400-420°C, where the solute element (Ca in liquid Li) reacted with the alloy substrate to produce a CaO coating.^{1,2} The objective of this study is to determine the optimal Ca-Li alloy for formation of the CaO coating from the liquidus temperature of binary alloys and experience obtained during their preparation.

SUMMARY

An electrically insulating coating at the liquid-metal/structural-material interface of a magnetic fusion reactor is required to prevent adverse currents generated by the magnetohydrodynamic (MHD) force from passing through the structural walls.^{3,4} Thin, homogeneous, electrically insulating CaO coatings can be produced on variously shaped surfaces of V-5%Cr-5%Ti by exposing the alloy at controlled times and temperatures to liquid Li containing Ca. Formation of Ca-Li alloys by dissolution of solid Ca in liquid Li in an Ar environment was investigated, and the exothermic heat of solution was found to be low, as indicated by minimal increases in temperature. The recommended composition of a liquid alloy for fabrication of this coating on reactor components is Li-82 wt.% Ca (44 at.% Ca), which has a liquidus temperature of $\approx 230^\circ\text{C}$. As the solute Ca in the liquid alloy is consumed during the coating process, the liquidus temperature of the alloy decreases. This coating technique can be applied to various shapes (e.g., inside/outside of tubes, complex geometrical shapes) because the coating is formed by liquid-phase reaction at $\approx 400^\circ\text{C}$. Cracks that form in the CaO coating during thermal cycling exhibit in-situ self-healing behavior at temperatures $\geq 360^\circ\text{C}$.²

INTRODUCTION

Corrosion resistance of structural materials, and the MHD force and its influence on thermal hydraulics, are major concerns in the design of liquid-metal cooling systems for fusion first-wall/blanket applications.³ Vanadium and V-base alloys (V-Ti or V-Ti-Cr) are leading candidate materials for structural applications in fusion reactors.⁵ Our recent work^{1,2} has focused on in-situ formation of CaO on V-5Cr-5Ti in liquid Li because the electrical resistivity of CaO is greater than that of other potential insulator candidates (e.g., AlN) and because CaO exhibits a higher thermodynamic stability than other oxides (Y_2O_3 , BeO, MgO, MgAl_2O_4 , $\text{Y}_3\text{Al}_2\text{O}_{12}$, etc.) in liquid Li.^{6,7} Thin, homogeneous, electrically insulating CaO coatings were produced on small specimens of V-5%Cr-5%Ti by controlling the exposure time, temperature, and composition of liquid Li containing dissolved Ca.² The objective of this study is to determine the optimal composition of the liquid Li-Ca alloy for use in coating various shapes such as the insides of tubes or irregular shapes in fusion reactor components.

According to the Ca-Li binary phase diagram shown in Fig. 1, Ca additions to liquid Li lower the melting point of Li-Ca alloys from 180.6°C (for pure Li) to 141°C for the eutectic mixture that contains 7.7 at.% Ca (≈ 32.5 wt.% Ca). The liquidus temperature of Ca-Li alloys increases slowly from 141 to 230°C as the concentration of Ca increases from ≈ 32.5 to 82 wt.%. The liquidus temperature then increases rapidly from 230 to 842°C , which is the melting point of pure Ca. From the standpoint of forming a thin homogeneous CaO coating on V-base alloys, a high concentration of Ca in liquid Li is desirable to provide a large source of Ca for the coating process, scavenge or "getter" nonmetallic impurities (e.g., O, N) in Li, and minimize incorporation of Li into the CaO film. Several Ca-Li compositions have been prepared, and

*Work supported by U.S. Department of Energy, Office of Fusion Energy Research, under Contract W-31-109-Eng-38.

melting/cooling cycles for the alloys have been obtained to verify the Ca–Li phase diagram in the range of interest. We also determined whether the initial heating cycle with mixtures of pure components produces an exothermic reaction that could present problems during application of the coating process to large components where a significant quantity of the liquid alloy is required.

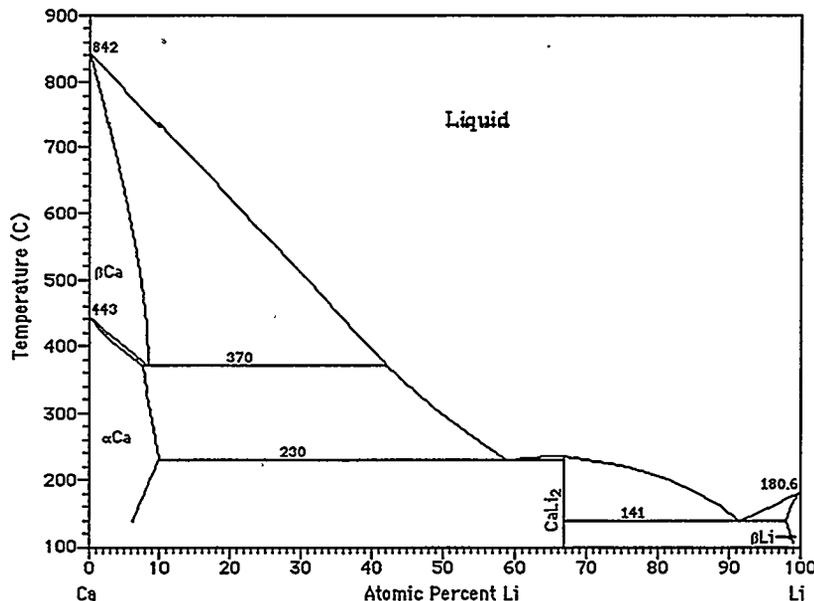


Figure 1. Ca–Li binary phase diagram

EXPERIMENTAL PROCEDURE

Figure 2 is a schematic drawing of the apparatus used in the heating/cooling experiments. Eight Ca–Li samples with 3–82 wt.% Ca (0.5–44 at.% Ca) were prepared from small (3–10 mm diameter) pieces of Ca and 3-mm-diameter Li wire. Isopropyl alcohol was used to rinse mineral oil from the Li wire. The Ca and Li were weighed and then loaded into a 150-mL Type 304 stainless steel (SS) container. Several methods were used to load the constituents (≈ 60 mL volume) into the apparatus in an attempt to minimize oxidation of the metals in air. Ar gas was purged in a plastic bag that held the container, and handling time was minimized. In some cases, the solid metals were placed sequentially in the container; in others, Li was placed at the bottom and Ca at the top of the container. After loading, the container was transferred to the SS chamber shown schematically in Fig. 2. Ar gas was purged simultaneously with a vacuum pump that purged air from the system. Heating was then started and the temperature was monitored with two thermocouples, which were initially located at the top of the mixture. Once fusion had occurred, one thermocouple was repositioned (lowered) and the temperature of the liquid phase was monitored. Cooling curves were obtained for various alloy compositions by removing the furnace from the SS chamber (Fig. 2) and slowing cooling the container in air. Thermal arrests were determined from cooling curves and the temperatures were compared with published phase diagrams^{8–10} for the Ca–Li system.

RESULTS AND DISCUSSION

Pure Li to 2.2 at.% Ca in Li. Cooling curves for pure Li and several alloys that contained 0–2.2 at.% Ca were obtained during furnace cooling. Only the liquidus temperature was revealed during cooling of pure Li and of the alloy with 0.5 at.% Ca. The liquidus and the eutectic point at 141°C were detected in alloys with 1.2, 1.6, and 2.2 at.% Ca.

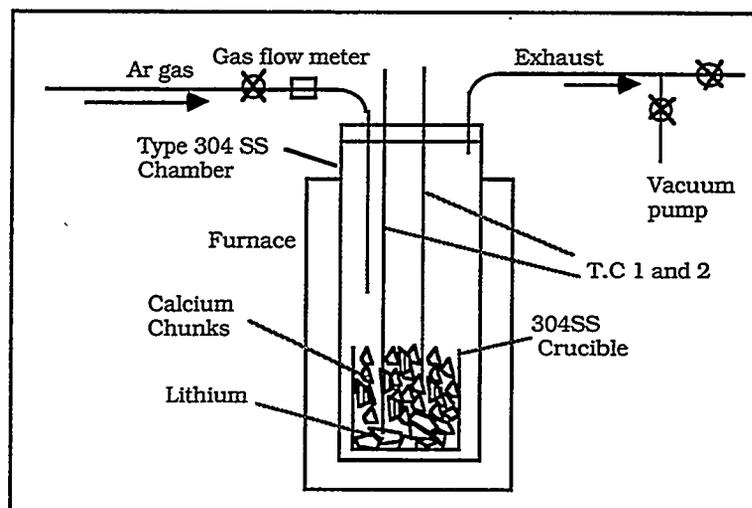


Figure 2. Schematic diagram of apparatus for heating/cooling experiments

4.1–33.3 at.% Ca in Li. Cooling curves for alloys that contained 4.1, 5.0, 7.7, 10.4, and 28 at.% Ca were obtained during furnace cooling, and the liquidus and eutectic temperatures were easily detected from breaks in the cooling curves.

33.3–100 at.% Ca. In this composition range, published Ca–Li phase diagrams do not agree with each other.^{8–10} Several heating/cooling cycles were performed on a Li–37 at.% Ca alloy. No appreciable heat was evolved during the initial heating cycle. Reproducible breaks in the cooling curves occurred at ≈ 230 and 142°C , temperatures that are indicative of formation of the CaLi_2 intermetallic phase and the eutectic temperature, respectively.

The temperatures and phases associated with thermal arrests during cooling of the various alloys are given in Table 1 and results for the Li-rich portion of the Ca–Li phase diagram determined in this study are shown in Fig. 3. The heat of solution of Ca in liquid Li is relatively small, as indicated by the thermocouple in the liquid during the initial heating cycle. The low-melting CaLi_2 intermetallic phase (mp $\approx 230^\circ\text{C}$) also exhibits a negligible exothermic heat of formation during initial fusion of Li (mp $\approx 180^\circ\text{C}$) in the presence of solid Ca, and during heating from the melting temperature to $\approx 230^\circ\text{C}$, where this phase is no longer stable.

CONCLUSIONS AND FUTURE STUDIES

Formation of Ca–Li alloys by dissolution of solid Ca in liquid Li in an Ar environment was investigated, and the exothermic heat of solution was found to be low, as indicated by minimal increases in temperature. Based on experience obtained during initial fusion of the alloys and the criterion for a high Ca concentration in the liquid to facilitate formation of a CaO coating on V–base alloys, we recommend an alloy that contains 82 wt.% Ca (44 at.% Ca) for fabrication of this coating on reactor components. The recommended alloy has a liquidus temperature of $\approx 230^\circ\text{C}$ and can be produced by charging weighed quantities of the two constituent metals into a stainless steel vessel and heating the mixture to $\approx 400^\circ\text{C}$ in an inert-gas environment to form a CaO coating on V–base alloys that are exposed to the liquid. Alternative methods for in-situ fabrication of a CaO electrically insulating coating on V–5Cr–5Ti in a liquid–Li environment can be envisioned. For example, liquid Li could be pumped at a low rate through a vessel containing solid Ca at $\approx 225^\circ\text{C}$ and the Ca-enriched alloy could then flow through a component to be coated at a higher temperature, at which the reaction process occurs at a significant rate. The coating, if it

deteriorates, can be restored by repeating this technique, or it can be maintained by using a low concentration of Ca in Li during normal operation of the system. The latter procedure would promote self-healing of defects that may form during thermal cycling of the coated structural material.

Table 1. Alloy composition and thermal arrest temperatures on cooling

Ca in Li		Thermal Arrest on Cooling
at. %	wt. %	°C
0.0	0.0	180
0.5	3.0	170, 150
1.2	6.5	174, 158
1.6	9.2	172, 141
2.2	11.5	169, 141
4.1	19.9	157, 141
5.0	23.3	165, 141
7.7	32.7	141
10.4	40.1	157, 142
28.0	69.2	210, 141
37.0	77.2	228, 142
100.0	100.0	842

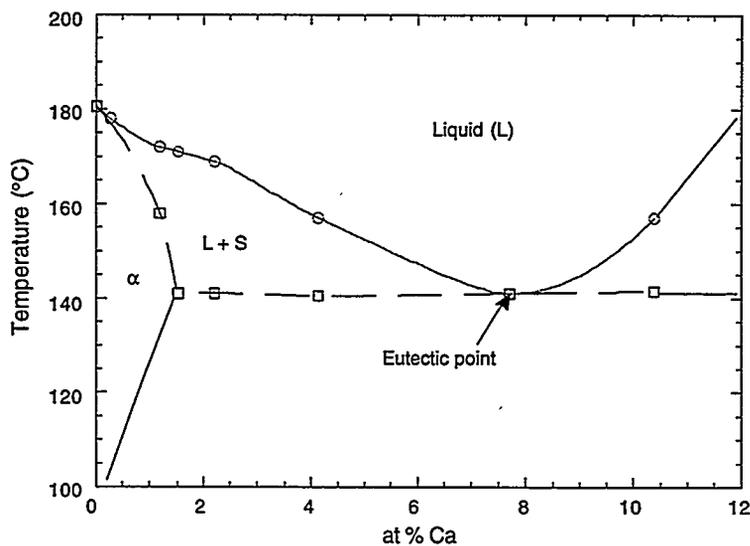


Figure 3. Li-rich region of Ca-Li phase diagram from this study

ACKNOWLEDGMENTS

- G. Dragel assisted in the liquid-Li experiments.

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